the lowest parts were near the ends—the two nodes. When the stationary wave was of the same length as the trough two mounds arose, one near each end, and so on.

It is suggested that the tidal ridges in estuaries and the chains of sand banks under the sea are formed in this way, by stationary or nearly stationary water waves, and that the sand dunes of the sea-shore and of the desert, and the clouds in a " mackerel sky " may be similarly the products of stationary air waves.

"The *Rôle* of Diffusion in the Catalysis of Hydrogen Peroxide by Colloidal Platinum." By GEORGE SENTER, Ph.D., B.Sc. (Lond.). Lecturer on Chemistry at St. Mary's Hospital Medical School. Communicated by Sir WILLIAM RAMSAY, K.C.B., F.R.S. Received March 7,—Read March 30, 1905.

According to a theory of reaction-velocities in heterogeneous systems recently put forward by Nernst,[*] the observed velocities are those with which diffusion and convection renew the reacting material at the boundary of the two phases, the actual chemical change at the boundary being very rapid in comparison. Nernst is of opinion that the same considerations apply to the catalytic decomposition of hydrogen peroxide by colloidal platinum and similar substances, but has not gone fully into the discussion of this particular class of heterogeneous reactions.

In a recent paper on the effect of poisons on the catalysis of hydrogen peroxide by hæmase,[†] I have discussed the probable mechanism of catalysis by colloidal particles, and have arrived at the conclusion that the experimental results obtained by Bredig and his pupils and by myself are best accounted for on Nernst's hypothesis.

In an important paper on this subject, Sand,[‡] starting from certain assumptions regarding the size and nature of the particles in a colloidal platinum solution, has calculated the minimum value of the velocity-constant (which we may call K_D) to be expected on Nernst's hypothesis, and finds that it is at least 16 times as great as the velocity-constant obtained experimentally by Bredig.[§] Hence, he concludes that Nernst's hypothesis does not apply to this particular reaction ; the observed velocity is really that of a chemical action.

[*] ' Zeitschrift für physikal. Chemie,' vol. 47, p. 52, 1904.
[†] ' Roy. Soc. Proc.,' vol. 74, p. 201, 1904.
[‡] ' Roy. Soc. Proc.,' vol. 74, p. 356 (1905).
[§] Bredig and Müller von Berneck, ' Zeit. für physikal. Chemie,' vol. 31, p. 258, 1899 ; Bredig and K. Ikeda, ' Zeit. für physikal. Chemie,' vol. 37, p. 1, 1901.

In another part of his paper Sand discusses the observation of Bredig that the reaction-velocity increases more rapidly than the concentration of the catalysor, and concludes that this can only be accounted for by increased convection owing to the brisker evolution of oxygen when large amounts of catalysor are present.

In the present paper it is shown that when K_D, which is a measure of the maximum rate at which hydrogen peroxide can be supplied to the particles by diffusion, is great in comparison with the observed velocity-constant K, the hydrogen peroxide concentration at the surface of the particles will be maintained by diffusion at a value which does not differ appreciably from the average concentration in the solution, so that increased convection will have practically no effect on the observed reaction-velocity. From this it follows that if, as Sand maintains, increased convection does modify the reaction-velocity considerably, K_D cannot be large in comparison with K, since convection can only modify the value of the former constant.

The question here considered is somewhat analogous to that of a slow chemical action succeeded by a rapid one. Under such circumstances it is the velocity of the slow action which is measured, and it is clear that an increase in the rate of the rapid reaction will have no effect on the observed velocity. It is not *a priori* evident that the same considerations apply to a slow chemical action, accompanied by rapid diffusion, since the constants of the two changes are not directly comparable, though both have reference to the rate of transference of hydrogen peroxide.

If K_D (as defined above) be n times as great as the velocity-constant K_0 of the chemical action at the surface of the colloidal particles, the concentration at the boundary will be maintained by diffusion at a value not less than $(n-1)/nth$ of the average concentration in the solution.

Let K be the observed velocity-constant and D, as defined below, have a value which does not differ appreciably from the average concentration C of hydrogen peroxide in the solution, then we have, for the rate of fall of concentration in the main bulk of liquid,

$$- dC/dt = KD \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (1).$$

Further, let K_0 be the velocity-constant of the chemical action, and C_r the concentration of peroxide close to the surface of any particle, then, if we assume that the reaction velocity is proportional to C_r, we find for the rate of fall of concentration at the boundary due to chemical action (which is of course equal to the observed rate of fall in the main bulk of liquid, since hydrogen peroxide is only removed at the boundary),

$$- dC/dt = K_0C_r \dots\dots\dots\dots\dots\dots\dots\dots \quad (2).$$

If this loss is just compensated by diffusion inwards towards the

particles, we find, from Sand's Equation (19), p. 367, that the amount removed by each particle in the time dt is

$$F dt = 4\pi k r \gamma (D - C_r) dt \quad \ldots\ldots\ldots\ldots\ldots \quad (3),$$

where k is the diffusion coefficient of hydrogen peroxide, r is the radius of the particle, and $\gamma = R/R - r$, where R is at such a distance from the particle that the concentration there is D, which does not differ appreciably from the average concentration in the solution.* The amount removed from unit volume containing N particles (where $4/3\pi r^3 N = v$) is N times as great, or

$$= \frac{4\pi k (D - C_r) \gamma v \times 3}{4\pi r^2} = \frac{12 k v \gamma (D - C_r)}{L^2} \quad \ldots\ldots\ldots\ldots \quad (4),$$

where $L = 2r =$ the diameter of a particle.

Hence

$$K = \frac{12 k v \gamma}{L^2} \left(1 - \frac{C_r}{D} \right) \quad \ldots\ldots\ldots\ldots\ldots \quad (5).$$

Further, since $KD = K_0 C r$, we have

$$K_0 = \frac{12 k v \gamma}{L^2} \left(\frac{D - C_r}{C_r} \right) \ldots\ldots\ldots\ldots\ldots \quad (6).$$

If K_0 is infinite (Nernst's hypothesis) $C_r = 0$, and from Equation (5) we obtain for K, which in this case is K_D, the value

$$K_D = 12 k v \gamma / L^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7),$$

which Sand shows is at least 16 times as large as the velocity-constant determined by Bredig. Hence, *if Sand's value for* K_D *be accepted*, we must conclude that C_r is not zero, and that experiment therefore does not justify Nernst's hypothesis.

From Equations (5) and (7) we can readily find the relation between C_r and D. If we deal with the case where K_D is 16 times as large as the observed velocity-constant K, it is obvious that

$$1 - \frac{C_r}{D} = \tfrac{1}{16}, \text{ or } C_r = \tfrac{15}{16} D.$$

In general, if K_D is n times as large as K, we have

$$C_r = \frac{n - 1}{n} D \quad \ldots\ldots\ldots\ldots\ldots \quad (8).$$

The way in which the observed velocity of a heterogeneous chemical reaction depends upon the relative values of the " diffusion " constant and the " chemical " velocity constant.—From Equation (8) we find that if K_D is great in comparison with K, the concentration at the surface of the particles, with a minimum of stirring, is practically equal to the average concentration in the solution. Since $K_0 C_r = KD$, it follows that in this case

* Sand, *loc. cit.*, p. 362.

the chemical velocity-constant K_0 is scarcely different from the observed velocity-constant K.

Just as in the case of successive inter-dependent chemical actions, there are, therefore, three cases to distinguish :—

(1) If K_0 is great in comparison with K_D (Nernst's hypothesis), the observed reaction-velocity depends only on K_D, it is that with which diffusion and convection bring the reacting material to the boundary.

(2) If K_0 and K_D are comparable in value, the observed velocity will depend on both, and will, consequently, be modified by alterations in either.

(3) If K_0 is small in comparison with K_D, the observed reaction-velocity depends only on K_0, and will, consequently, not be affected by such changes as stirring may produce in the value of K_D.

So far as we have gone, it would seem that the platinum catalysis of hydrogen peroxide is an example of Case (3).

The reaction-velocity increases much more rapidly than the Catalysor concentration.—Bredig* has found that, on doubling the amount of his catalysor, the reaction-velocity is trebled instead of merely being doubled, as one would expect if the catalysor particles act independently of one another, and Sand, apparently with good reason, has suggested that this is due to convection currents set up by the rapid evolution of oxygen bubbles in solutions containing large quantities of catalysor. This view as to the great effect of convection currents cannot, however, be easily reconciled with the conclusion arrived at above, that we are dealing with a "chemical" reaction-velocity. We have seen that, in the case considered, C_r, with a minimum of stirring, is $\frac{15}{16}$ of the average concentration in the solution. The effect of stirring would be to shorten the diffusion-layer, and bring C_r nearer to the average concentration; but it is clear that the greatest possible alteration of the reaction-velocity from this cause will only amount to $\frac{1}{15}$ of its value, which is quite insufficient to account for Bredig's results.

In searching for an explanation of this difficulty, we must first consider what evidence there is for the suggestion that the want of proportionality between K and the catalysor concentration is due to the disturbing effect of convection currents. If this is not the case—if an explanation on chemical grounds can be found for the deviation in question—then we must regard the observed velocity as in all probability a chemical velocity. If, on the other hand, the want of proportionality is due to the effect of convection in modifying the reaction-velocity, it is clear that K_D cannot be great in comparison with K, and we must search for a possible error in the assumptions which have led to this conclusion.

The Part Played by Convection Currents.—As Sand has pointed out, " the fact that K increases more rapidly than the catalysor concentra-

* Bredig and Müller von Berneck, *loc. cit.*, p. 312.

tion can only be accounted for by supposing that the process taking place on the surface of a particle influences that of its neighbours by some non-chemical means," and it is difficult to imagine any other way in which this can be effected than by the production of convection currents. Sand suggests that these currents are set up in the liquid by the bubbles of oxygen evolved, but this cannot be regarded as a complete explanation of the observed facts. On this view we would expect K to increase with increasing peroxide concentration (owing to the more rapid evolution of oxygen), but this is not the case. It has been found that K decreases,* though only to a small extent, with increased peroxide concentration. Further consideration shows, however, that this apparent contradiction can be satisfactorily accounted for on the convection hypothesis.

We must, as a matter of fact, consider three possible ways in which K may be affected by the processes in question :—

(1) The particles themselves are in Brownian motion ;† they are continually moving into fresh portions of the solution, and thus tend to keep a constant concentration outside the adherent layer through which diffusion is taking place. Further, owing to their motion, they stir the liquid as a whole, and thus, with increasing concentration, the average thickness of the layers on all the particles would be lessened, so that K would increase more rapidly than the catalysor concentration.

(2) Owing to evolution of bubbles of oxygen in the stronger solutions, and consequent stirring of the liquid, the diffusion path would be shortened, and K, as we have already seen, would increase more rapidly than the platinum concentration.

(3) The formation of bubbles on the surfaces of the particles would interrupt the diffusion-layer and tend to retard the action. This process on one particle would not, however, affect that on another, so that, *as far as this effect alone is concerned,* the reaction-velocity would be proportional to the platinum concentration. In solutions containing the same amount of catalysor and different peroxide concentrations, we would expect this disturbing cause to increase with the peroxide concentration, so that the greater velocity to be expected from increased stirring might be more than neutralised by the cause just mentioned. We have thus a simple explanation of the observed fact that K decreases slightly with increase of H_2O_2. The fact that K increases considerably during the action, which has up to the present not been satisfactorily accounted for,‡ is probably due to a combination of the two convection effects just discussed.

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* Bredig and Ikeda, *loc. cit.,* p. 4.

† Senter, *loc. cit.,* p. 213.   Compare Spring, ' Bull. Soc. Chim. Belg.,' vol. 19, p. 219, 1900.

‡ Compare Bredig and Ikeda, *loc. cit.,* p. 5 ; Engler and Wöhler, ' Zeit. Anorg. Chemie,' vol. 29, p. 13, 1901.

In solutions of hydrogen peroxide so dilute that the oxygen evolved would be insufficient to saturate the solution, we would expect K to be proportional to the catalysor concentration, and independent of the peroxide concentration. This has not been directly determined for platinum, but Sand,* by collating results in different parts of Bredig's paper, has shown that in solutions containing very little platinum, K is approximately proportional to the platinum concentration. It is strictly true of the hæmase catalysis; † only when the evolved oxygen is more than sufficient to saturate the solution do deviations from the simple logarithmic formula appear.

The fact that *all* the observations in the platinum and hæmase catalysis of hydrogen peroxide are thus satisfactorily accounted for on the hypothesis of convection currents, seems a strong argument in favour of the view that the latter play a considerable part in the action.

Possible errors in the assumptions used in calculating K_D.—If the above views as to the part played by convection currents are accepted, we must investigate the assumptions which have led to the conclusion that the value of K_D is great in comparison with that of K. Sand arrived at this result by substitution of probable minimum values for k and v, and a maximum value for L, the diameter of a particle, in Equation (5), $K_D = 12 \, kv\gamma/L^2$.

There would seem to be at least three possible sources of error in the calculation of a numerical value for K_D. (1) The value (10^{-5} cm.^{2} per sec.) assumed for k, the coefficient of diffusion of hydrogen peroxide, may be too large. (2) The average diameter L of the particles may be greater than the maximum value assumed by Sand (0.5μ). (3) Only part of the platinum surface may be active towards hydrogen peroxide; the value taken for v may thus be too large.

These three possibilities will now be shortly considered :—

(1) Although the diffusion coefficient of hydrogen peroxide has not been determined, there can be very little doubt, from the values obtained with substances of similar molecular weight, that the value assumed for k is not too large, so that an error from this cause is very unlikely.

(2) *The size of the particles.*—Since, according to Equation (7) K_D varies inversely as the square of the diameter of the particles, the velocity calculated on Nernst's hypothesis would correspond with the velocity actually observed if the average diameter of the particles be four times the maximum value (0.5μ) assumed by Bredig and Sand. Bredig‡ mentions that his solutions showed no suspended particles when examined under a microscope capable of detecting objects of the diameter 0.2μ. Although it ought to be borne in mind that particles

* *Loc. cit.*
† Senter, ' Zeit. physikal. Chemie,' vol. 44, p. 257, 1903.
‡ ' Anorganische Fermente,' Leipzig, 1901, p. 21.

in motion may not be so readily detected as stationary particles,* yet the uncertainty from this cause would be least in the case of large particles, so that it seems very improbable that particles of the diameter μ could escape detection under the above conditions.

Zsigmondy and Siedentopf† have investigated the magnitude of the particles in colloidal solutions of gold prepared by reduction ; they find many particles of the diameter $1/100\mu$ and others still smaller.   Stöckl and Vanino‡ have independently arrived at the same result.   So far as I am aware, colloidal solutions, prepared by Bredig's method, have not been examined by Zsigmondy and Siedentopf's method, but it does not seem probable that such solutions would differ markedly, as regards the magnitude of the particles, from those prepared by reduction.

It may, therefore, be concluded that the want of agreement between K_D and K cannot be accounted for by too low a value having been taken for the magnitude of the particles.

(3) *The suggested inactivity of part of the platinum surface towards hydrogen peroxide.*—Equation (7) has been derived on the assumption that all the particles are active towards hydrogen peroxide.   If only some of the particles are thus active, the total reacting surface, which is proportional to v for equal particles, would be diminished, and thus K_D would attain a value more nearly coresponding to K.   (It should also be noted that v and consequently K_D would be diminished by the process discussed under the third heading in the section on convection, p. 570, but this effect would, in any case, be small and would completely disappear for solutions in which oxygen is not evolved in bubbles, so that we cannot account in this way for the difference between K_D and K).   Nernst§ has already suggested the possibility that part of the platinum is inactive, and some positive evidence to this effect is to be found in papers by Bredig and Fortner‖ and by Liebermann.¶   The first two investigators found that the palladium catalysis of hydrogen peroxide is greatly accelerated by previous treatment of the palladium with hydrogen, and the same is true, though to a much smaller extent, of the platinum catalysis.   The latter result has been confirmed by Liebermann. Bredig** has also found that platinum which has been poisoned with CO is more active after recovery from the poison than platinum which has not been so treated.

* The limit of visibility under the microscope will probably depend upon the number of the particles present in a given volume, as well as on the nature and magnitude of their motion.

† 'Zeit. für Elektrochemie,' vol. 8, p. 686, 1902.

‡ 'Zeit. für physikal. Chemie,' vol. 30, p. 99, 1899.   Compare also Lobry de Bruyn, 'Receuil Travaux Chim. Pays-bas,' vol. 19, p. 251, 1900.

§ *Loc. cit.*, p. 55.

‖ 'Berichte d. deut. chem. Ges.,' vol. 37, p. 805, 1904.

¶ 'Berichte d. deut. chem. Ges.,' vol. 37, p. 1519, 1904.

** 'Anorg. Fermente,' p. 79.

The cause of this increased activity must be, for the present, largely a matter of speculation. It may possibly be due to the breaking up of aggregates of particles and consequent increase of the reacting surface, but a more probable explanation is that the surfaces are partly freed from some impurity which prevents action on the peroxide. The suggestion may be made that this surface impurity is platinous oxide. It has been shown by Mond, Ramsay and Shields,* and by Wöhler,† that this oxide results when platinum is heated in air, and, having regard to the method of preparation of Bredig's solutions, it is to be expected that the platinum will be partly oxidised. This is supported by the observation of Bredig that a trace of his colloidal platinum is dissolved by sulphuric acid. Engler and Wöhler‡ have shown that platinous oxide acts much less energetically on hydrogen peroxide than platinum itself.

It seems probable that, as many investigators have suggested, an intermediate oxide of platinum is formed in the platinum catalysis of hydrogen peroxide, but most likely a higher oxide, perhaps PtO_2, which can react rapidly with the peroxide. This would correspond with Manchot's§ explanation of the great accelerating effect of ferrous salts on oxidations as compared with ferric salts. He has shown that the action proceeds by intermediate formation of a higher oxide of iron, and that the catalytic effect is much lessened when part of the iron has changed to the ferric condition.

Whether this suggestion applies or not, it is clear from what has been given above that there is reason for supposing that the entire platinum surface is not active under ordinary conditions, and this seems the most probable explanation of the difference between K_D as calculated by Sand, and K the observed velocity-constant.

Summary and Conclusion.

It has been shown that the deviations from the simple logarithmic formula in the catalytic decomposition of hydrogen peroxide by colloidal platinum are probably due to disturbances caused by convection currents. It has further been shown that when the velocity-constant calculated on Nernst's diffusion hypothesis is great compared with the chemical velocity-constant, increased convection can produce no appreciable effect on the observed reaction-velocity.

In the case under consideration, therefore, since increased convection modifies the observed reaction-velocity, there must be some error in the assumptions which lead to the conclusion that the diffusion velocity-

* ' Zeit. physikal. Chemie,' vol. 25, p. 685, 1898.

† ' Zeit. Anorg. Chemie,' vol. 36, p. 3475 (1903).

‡ ' Zeit. Anorg. Chemie,' vol. 29, p. 13, 1901.

§ ' Annalen der Chemie,' vol. 325, p. 93, 1902.

constant is great in comparison with the chemical velocity-constant. This error is probably to be found in the assumption that the whole surface of the platinum is, under ordinary conditions, active towards hydrogen peroxide.

We are not entitled to assume, from the above considerations, that Nernst's hypothesis is true for the platinum catalysis, but only that the diffusion-velocity is not great in comparison with the chemical velocity (Cases 1 and 2, p. 569). Other considerations, however, such as the small value of the temperature coefficient, make it probable that the above hypothesis does apply to this particular action. Further support for this view may, perhaps, be found in the fact that the deviations from the simple logarithmic law in catalysis by platinum have their exact analogy in the hæmase catalysis. On the " chemical " velocity hypothesis it would seem rather remarkable that two catalysors of so different origin should show exactly similar behaviour, but this becomes at once intelligible on Nernst's hypothesis, according to which the chemical action plays quite a secondary part in the re-action-velocities in question.

In conclusion, I wish to acknowledge my obligations to Professor A. W. Porter and Dr. Sand, with whom I have had the advantage of discussing the subject-matter of the present paper.